ZEOLITE-BASED MERCURY SORBENT-
LABORATORY TESTING AND MODELING

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INTRODUCTION

Mercury is one of the 11 toxic metals recognized by the Title III of the Clean Air Act Amendments as Hazardous Air Pollutants and has received special attention because of its high volatility combined with high toxicity and bioaccumulation. In the United States 21% of the total mercury emissions are attributed to coal-fired utility boilers.[1] The forms of mercury vapor in power plant flue gases are elemental Hg and oxidized Hg (probably $HgCl_2$, and in some cases, HgO), with elemental mercury being the predominant form.[2-6]
Generally, $HgCl_2$ can be removed from the flue gases easier than elemental Hg, either through wet scrubbing, dry injection or fixed bed using activated carbon.[3-10] However, removal of elemental mercury is more challenging, since it is practically insoluble in water and can be removed to a certain extend with expensively treated activated carbons

PSI has developed and tested mercury sorbents for enhanced removal of both elemental and oxidized mercury based on a natural zeolite. The sorbents were injected to mercury containing flue gases from combustion of coal, which were at 150 or 230°C. Three different forms of this zeolite were used, plain zeolite and two types of modified zeolited treated with proprietary agents.

EXPERIMENTAL

Combustion of coal took place at PSI's electrically heated Entrained Flow Reactor (EFR). This apparatus, which can achieve a maximum gas temperature of 1723 K, has been used extensively on many of PSI's combustion research projects. Fuel, air, other gases and coal are injected at the top of the reactor. The combustion section is an externally heated ceramic tube that is 8.57 cm in internal diameter and 158 cm in length.

Once the flue gas exited the furnace, it entered a quartz tubular reactor where sorbent injection took place. The reactor temperature was kept constant to 130 or 200°C. To ensure that no additional mercury removal took place downstream the reactor, the flue gases passed through a series of particulate removal devices, including an impactor, two cyclones and finally a filter, see Fig. 1. The particle removal devices were kept at about 150°C.

After leaving the filter assembly, the gas stream passed into a series of impingers designed to collect any mercury left in the flue gases and determine the mercury species, as specified by Ontario Hydro Method. The sorbent injection system consisted of a syringe with the sorbent loaded on driven by a syringe pump into a tube. The air flowing in the tube was used to carry the sorbent. The injection rate was controlled by the speed of the syringe pump.

Coal was burned in the EFR to more closely approach the conditions found in power plant flue gases. For this program, a bituminous coal, Pittsburgh seam, was used. The mercury content of the coal as determined by Neutron Activation Analysis is 0.11 ppm. To maintain 10-70 $\mu g/m^3$ levels of Hg concentration, a mercury laden stream of oxygen was added to the top of the EFR.

Two types of treated zeolite were used, TZ1 and TZ2, and also untreated zeolite, UZ, with particle size in the range of 1 to 5 μm. In addition, a high-surface-area activated carbon, AC, CL-213, from Barneby and Sutcliffe was used as a comparison.

The normal operating conditions were:
- Coal flow rate: 1.7 g/min
- Furnace temperature: 1700 K
- Equivalence ratio: 1.2
- Mercury reactor residence time: 2-3 s
- Mercury reactor temperature: 130 and 230°C.

At the end of each experiment six samples were collected and analyzed for mercury concentration: the ash/sorbent from the impactor and the two cyclones, the filter with any collected material, the three liquid samples from the Ontario-Hydro sampling train and the rinse of the glassware.
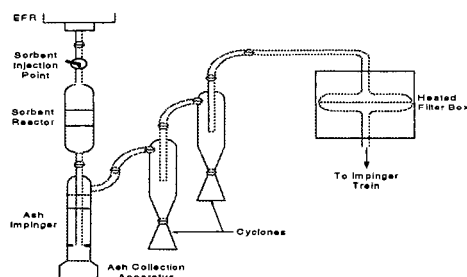

Figure 1. Sorbent injection, reactor and particulate collection apparatus for sorbent injection experiments.

RESULTS

Sorbent Injection Data

Figure 2 shows a plot of mercury capture as a function of sorbent:Hg ratio. For all sorbents capturing efficiency increased with sorbent to mercury ratio. The removal efficiencies of a treated zeolite (TZ2) and activated carbon (AC) were well over 90% even for modest sorbent to Hg ratios in the range of 25,000. The other treated zeolite (TZ1) exhibited removal efficiencies 45-55% for average sorbent to mercury ratios and up to 85% for high sorbent to mercury ratios, of about 90,000. The temperature did not appear to affect the capturing efficiency of the sorbents.
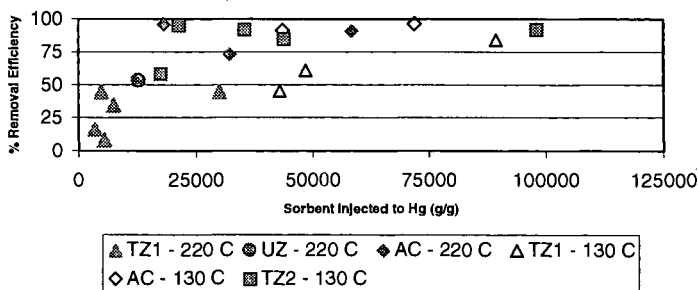
Figure 2. Mercury removal efficiency as a function of sorbent to mercury ratios.

Figure 3 shows the amount of mercury removed per unit mass of sorbent (sorbent utilization) plotted against the sorbent to mercury ratio present in the effluent stream. As the sorbent to mercury ratio increases, the amount of mercury removed per unit mass of sorbent decreases for all sorbents.

Figure 4 shows the percentage of oxidized mercury in the remaining mercury (was not removed by the sorbents) as a function of sorbent to mercury ratio. For low sorbent to mercury ratios, oxidized mercury decreases from 25% to less than 5% at a sorbent to mercury ratio of 25,000. Then it increases to about 50% for a sorbent to mercury ratio of 50,000 and decreases to less than

Mercury mass balance closure was determined for all runs by adding the mercury from each of the analyzed samples and dividing by the sum of the theoretical mercury from the combustion of the coal and the added mercury from the permeation tube as determined by the Jerome analyzer. The mercury mass balance for most of the runs was in the range of 70-110%.
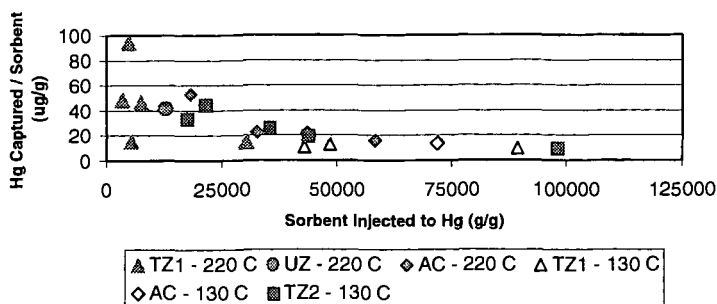

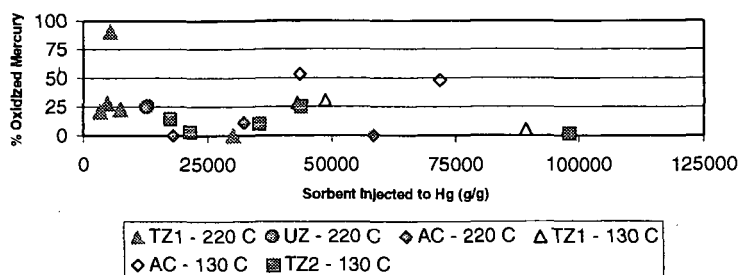**Figure 3.** Sorbent utilization as a function of sorbent to mercury ratio.

Figure 4. Percentage of oxidized mercury in the remaining (not removed) mercury.

Baseline Runs
In order to characterize the experimental apparatus and explain experimental data, three types of baseline runs were conducted. In all cases additional mercury was added to the system.
  (A) No coal combustion took place and no sorbent was injected. The purpose of these experiments was to determine the amount of mercury that may be lost while flowing through the furnace.
  (B) No coal combustion took place but treated zeolite was injected. The purpose of these experiments was to determine the amount of mercury captured by the treated zeolite when no coal combustion products are present.
  (C) Coal combustion took place but no sorbent was injected. The purpose of these experiments was to measure the amount of mercury removed by the fly ash alone.

For baseline A runs, over 98% of the total amount of mercury injected is recovered in the impingers at the end of the baseline A runs. This indicates that there is no substantial amount of mercury lost or unaccounted for while flowing through the furnace. Also for these runs, greater than 95% of the mercury is collected as elemental mercury.

In baseline type B, TZ1 was injected into the sorbent reactor at 130°C (266°F), with no coal combustion taking place. The sorbent to Hg ratio was 89,000 and the removal efficiency was 85 %. Similar removal efficiencies of the same sorbent were found in presence of combustion products, see Fig. 2.

Removal efficiencies from ash, as measured in baseline C runs (ash baseline) are shown in Fig. 5. Removal efficiencies increase from about 35% to 65% as the ash to mercury increases from 50,000 to 120,000.
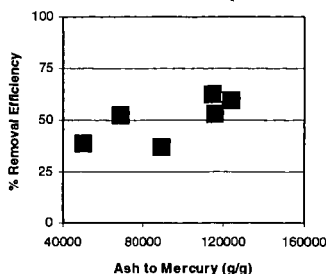
Figure 5. Ash removal efficiency as a function of ash to mercury ratio.

Modeling

The impact of speciation of mercury on activated carbon performance has been quantified in laboratory fixed bed experiments[11] and these data can be applied to models for the performance of sorbents in duct injection mode.[12] Figure 6 shows a calculation of the mercury removal at 130 °C for 5 micron activated carbon particles and a mercury concentration of 35 μg/m^3. The calculation assumes plug flow conditions with a two second residence time. Using fixed bed data to determine the reactivity of a single activated carbon to elemental mercury and mercury chloride, the figure shows the removal efficiency for both species. Mercury chloride shows a higher removal rate for a fixed sorbent to mercury ratio. Figures 2 and 6 show a good agreement between theory and experiments.
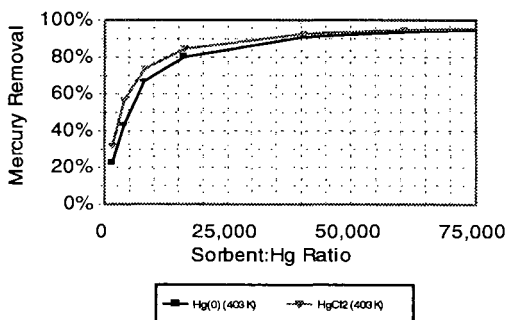

Figure 6. Calculated mercury removal for 2 seconds residence time at 130°C, assuming 5 micron activated carbon and concentration of 35 μg/m^3.

DISCUSSION

The ash baseline runs, see Fig. 5, indicate that ash can remove substantial amounts of mercury, as long as sorbent is not present. However, in the presence of sorbent, ash appears to lose its ability to remove mercury. If we assume that the removal efficiency of ash is independent of the presence of sorbent, then the removal efficiencies in presence of sorbent would have to be much higher than those indicated in Fig. 2.

Results indicate that oxidation of mercury takes place in presence of ash and/or sorbent. Baseline A suggests that only 5% of the injected mercury is oxidized in the furnace when no combustion products are present. However, in the presence of combustion products and/or sorbents, oxidized mercury can be 25-50% of the remaining (not removed) total mercury. Taking into account the removal efficiency, there is a net production of oxidized mercury from elemental in those experiments.

Physical Sciences Inc. (PSI) is developing mercury sorbents using a zeolite material treated with proprietary agents for improved capture of elemental as well as oxidized mercury. The performance of these sorbents was compared with that of activated carbon tested at similar conditions. To identify removal mechanisms of mercury, the mercury removal process was modeled using an adsorption/diffusion model.

The mercury removal efficiencies of sorbents varied in the range of 45-96% for sorbent to Hg ratios in the range of 5,000-96,000. A treated zeolite (TZ2) and the activated carbon exhibited removal efficiencies well over 90% at modest sorbent to Hg injection ratios of 25,000.The sorbent utilization, expressed as the amount of mercury removed per unit mass of sorbent, decreased from 80 μg Hg/g of sorbent to 6 μgHg/g of sorbent as the sorbent to Hg ratio increased from 5000 to 96,000. When no sorbent was injected, ash did remove some mercury, but in the presence of sorbent the role of ash in mercury removal appeared to diminish, presumably due to the higher reactivity of the sorbent with respect to the ash. Also, when no sorbent was present ash appeared to oxidize mercury, but in the presence of sorbent no substantial oxidation of mercury appeared to have taken place.

Results from the modeling effort suggest that at low sorbent injection rates mercury removal is highly influenced by adsorption kinetics. At higher concentrations diffusion becomes more pronounced. Also, modeling results indicate that most mercury is removed very shortly after injection, while long injection times do not substantially increase the removal rate.

ACKNOWLEDGMENTS

REFERENCES

1. *Mercury Study Report to Congress*, EPA-452/R-96-001g, 1996.
2. Tumati, P.R.; DeVito, M.S. "Partitioning Behavior of Mercury During Coal Combustion," presented at the Joint ASME/IEEE Power Gen. Conf., Kansas City, KS (October 1993).
3. DeVito, M.S.; Jackson, B.L. "Trace Element Partitioning and Emissions in Coal-Fired Utility Systems," presented at the 87th Annual Meeting and Exposition of the Air and Waste Management Association, Cincinnati, OH (June 1994).
4. Meij, R. "Distribution of Trace Species in Power Plant Streams: A European Perspective," presented at American Power Conf., Chicago (April 1994).
5. Nordin, A.; Schager, P.; Hall, B. "Mercury Speciation in Flue Gases: A Comparison of Results from Equilibrium Calculations with Results from Laboratory Experiments," Swedish Flame Days, Turkoo, Finland (September 1990).
6. Young, B.C.; Miller, S.J.; Laudal, D.L. "Carbon Sorption of Trace Mercury Species," proceedings of the 11th Annual Pittsburgh Coal Conference (September 1994), pp. 575-580.
7. Gorishi, B.; Gullet, B.K. "Sorption of Mercury Species by Activated Carbon and Calcium Based Sorbents: Effect of Temperature, Mercury Concentration and Acid Gases," *Waste Management & Research* **1998**, *6*, 582-593.
8. Guijarro, M.I.; Mendioroz, S.; Munoz, V. "Effect of Morphology of Sulfurized Materials in the Retention of Mercury from Gas Streams," *Ind. Eng. Chem. Res.* **1998**, *37*, 1088-1094.
9. Mendioroz, S.; Guijarro, M.I.; Bermejo, P.J.; Munoz, V. "Mercury Retrieval from Flue Gas by Monolithic Absorbents Based on Sulfurized Sepriolite," *Environ. Sci. Technol.* **1999**, *33*, 1697-1702.
10. Karatza, D.; Lancia, A.; Musmarra, D. "Fly Ash Capture of Mercuric Chloride Vapors From Exhaust Combustion Gas," *Environ. Sci. Technol.* **1998**, *32*, 3999-4004.
11. Carey, T.R., Hargrove, O.W., Richardson, C.F., Chang, R., and Meserole, F.B., "Factors Affecting Mercury Control in Utility Flue Gas Using Sorbent Injection," Paper 97-WA72A.05, presented at Air & Waste Management Association" 90th Annual Meeting, June 8-13, 1997, Toronto, Ontario, Canada.
12. Meserole, F.B., Chang, R., Carey, T.R., Machac, J., Richardson, C.F., "Modeling Mercury Removal by Sorbent Injection," *J. Air Waste Manage. Assoc.,* **1999**, *49*, 694-704.